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Signed, this 15<sup>th</sup> day of August 2002

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# FEDERAL REPUBLIC OF GERMANY

## Certificate of Priority for Filing of a Patent Application

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The attached papers are a true and accurate reproduction of  
the original documents for this patent application.

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On behalf of the President  
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Faust

**Rubber mixtures with polyurea fillers**

5 The present invention provides rubber mixtures of rubber and specific polyurea fillers, a process for preparing the rubber mixtures according to the invention and use of the rubber mixtures to prepare rubber vulcanisates and moulded items of all types, in particular tyres with low specific weights and low dynamic damping, as well as the vulcanisates and moulded items themselves.

10 To lower the rolling resistance and to reduce the weight of tyres, a number of measures have been described in the prior art, including the use of organic fillers instead of carbon black, such as e.g. rubber gels (EP-A 405 216 and DE-A 4 220 563), starch (EP-A 795 581) or cellulose fibres (EP-A 905 186).

15 US-A 5 223 599 describes tyres made from polyurea/polyurethane. The polyurea/polyurethanes are not used as fillers here, but as elastomers and therefore, naturally, have quite different physical properties and a very much lower resistance to hydrolysis than the rubbers and vulcanisates in the present invention, which possess no hydrolysable rubber chains.

20 The preparation and use of polyureas is also described in the Encyclopedia of Polymer Science and Engineering, John Wiley, New York 1988, vol. 13, pages 212-243. However, no indication is given in that book about the use of specific polyureas as fillers in rubbers.

25 It has now been found that rubber mixtures and vulcanisates with especially good mechanical and dynamic properties can be prepared from rubbers and specific polyureas with a certain particle size, and these are exceptionally suitable for preparing highly reinforced moulded items, in particular tyres and industrial rubber articles.

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The present invention therefore provides rubber mixtures consisting of a rubber and of 1 to 300, preferably 5 to 150 parts by wt., with respect to 100 parts by wt. of rubber, of a polyurea filler with a particle size of 0.001 to 500  $\mu\text{m}$ , preferably 0.01 to 100  $\mu\text{m}$ , particularly preferably 0.01 to 20  $\mu\text{m}$  and optionally other rubber auxiliary substances and cross-linking agents.

The invention also provides a process for preparing polyurea-filled rubber mixtures which is wherein at least one polyisocyanate reacts with at least one polyamine and/or water at temperatures of  $-50^{\circ}\text{C}$  to  $250^{\circ}\text{C}$ , preferably  $20^{\circ}\text{C}$  to  $150^{\circ}\text{C}$ , in a solvent with precipitation of the polyurea, a solution of a rubber is mixed with the polyurea obtained and the solvent is removed.

The solvent used during preparation of the rubber mixtures according to the invention is preferably removed by steam distillation.

In a particularly preferred embodiment, the polyurea is prepared by reacting a polyisocyanate with a polyamine in a rubber solution or in an emulsion of a rubber solution and water so that rubber mixtures according to the invention can be prepared without using an additional solvent.

The polyureas are prepared by reacting polyisocyanates with polyamines and/or water and have the particle sizes mentioned above and melting or decomposition points of  $\geq 200^{\circ}\text{C}$ , preferably  $\geq 220^{\circ}\text{C}$ . Their glass transition temperatures, if they exist, are higher than  $50^{\circ}\text{C}$ , preferably higher than  $100^{\circ}\text{C}$ .

Suitable polyisocyanates for preparing the polyureas are e.g. hexamethylene diisocyanate (HDI), toluene diisocyanate (TDI), 4,4'-diisocyanatodiphenylmethane (MDI), polymethylene-polyphenyl isocyanate (PMDI), naphthalene diisocyanate (NDI), 1,6-diisocyanato-2,2,4-trimethylhexane (IPDI), tris-(4-isocyanato-phenyl)-methane, tris-(4-isocyanato-phenyl) phosphate, tris-(4-isocyanato-phenyl) thiophosphate and also

oligomerisation products which have been obtained by reaction of the low molecular weight diisocyanates mentioned and diols or polyalcohols, in particular ethylene glycol, 1,4-butanediol, 1,6-hexanediol, trimethylolpropane or pentaerythritol and have a residual concentration of free isocyanate groups. Furthermore, oligomerisation products which have been obtained by reacting the low molecular diisocyanates mentioned with hydroxyl group-containing polyesters such as e.g. polyesters based on adipic acid and butanediol and hexanediol with molecular weights of 400 to 3,000 or by reacting with hydroxyl group-containing polyethers such as polyethylene glycols, polypropylene glycols, polytetrahydrofurans with molecular weights between 150 and 3,000 and have a residual concentration of free isocyanate groups, also oligomerisation products which have been obtained by reacting the low molecular weight diisocyanates mentioned with water or by dimerisation or trimerisation such as e.g. dimerised toluene diisocyanate (Desmodur TT) and trimerised toluene diisocyanate, isocyanate group-containing aliphatic polyuretdiones, e.g. those based on isophorone diisocyanate and have a residual concentration of free isocyanate groups. Preferred concentrations of free isocyanate groups are 2.5 to 50 wt.%, preferably 10 to 50 wt.%, particularly preferably 15 to 50 wt.%. These types of polyisocyanates are known and are commercially available. See, on this topic, Houben-Weyl, Methoden der organischen Chemie, vol. XIV, pages 56-98, Georg Thieme Verlag, Stuttgart 1963, Encyclopedia of Chem. Technol., John Wiley 1984, vol. 13, pages 789-818, Ullmann's Encyclopedia of Industrial Chemistry, VCH, Weinheim, 1989, vol. A14, pages 611-625 and the commercial products in the Desmodur and Crelan series (Bayer AG).

Suitable polyisocyanates are also blocked polyisocyanates which can react with polyamines under the reaction conditions mentioned. Included here are all the polyisocyanates already mentioned, wherein the isocyanate groups are each blocked with suitable elimination groups which are eliminated at elevated temperature and release the isocyanate groups again. Suitable elimination groups are in particular caprolactam, malonates, phenol and alkylphenols such as e.g. nonylphenol, and also imidazole and sodium hydrogen sulfite. Particularly preferred are caprolactam, malonate

and alkylphenol-blocked polyisocyanates, in particular those based on toluene diisocyanate or trimerised toluene diisocyanate. Preferred concentrations of blocked isocyanate groups are 2.5 to 30 %. These types of blocked polyisocyanates are known and are commercially available. See, on this topic, Houben-Weyl, Methoden der  
5 organischen Chemie, vol. XIV, pages 56-98, Georg Thieme Verlag, Stuttgart 1963 and the commercial products in the Desmodur and Crelan series (Bayer AG).

Particularly preferred polyisocyanates are hexamethylene diisocyanate (HDI), toluene diisocyanate (TDI), 4,4'-diisocyanatodiphenylmethane (MDI), polymethylene-  
10 polyphenyl isocyanate (PMDI), 1,6-diisocyanato-2,2,4-trimethylhexane (IPDI), and oligomerisation products which have been obtained by reacting the low molecular weight diisocyanates mentioned with water or with diols or polyalcohols, in particular ethylene glycol, 1,4-butanediol, 1,6-hexanediol, trimethylolpropane and pentaerythritol, and have a residual concentration of free isocyanate groups, and also oligomerisation  
15 products which have been obtained by dimerisation or trimerisation such as dimerised toluene diisocyanate (Desmodur TT) and trimerised toluene diisocyanate, isocyanate group-containing aliphatic polyuretdiones, e.g. based on isophorone diisocyanate, and have a concentration of free isocyanate groups of 2.5 to 50 wt.%, preferably 10 to 50 wt.% and particularly preferably 15 to 50 wt.%.

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Very particularly preferred are hexamethylene diisocyanate (HDI), toluene diisocyanate (TDI), 4,4'-diisocyanatodiphenylmethane (MDI), polymethylene-polyphenyl isocyanate (PMDI) and/or 1,6-diisocyanato-2,2,4-trimethylhexane (IPDI).

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Suitable polyamines are aliphatic diamines and polyamines such as hydrazine, ethylene diamine, 1,2-propylene diamine, 1,3-propylene diamine, 1-amino-3-methylamino-propane, 1,4-diaminobutane, N,N'-dimethylethylene diamine, 1,6-diaminohexane, 1,12-diaminododecane, 2,5-diamino-2,5-dimethylhexane, trimethyl-1,6-hexane diamine, diethylene triamine, N,N',N''-trimethyldiethylene triamine, triethylene tetramine,  
30 tetraethylene pentamine, pentaethylene hexamine, polyethylene imine with molecular

weights between 250 and 10,000, dipropylene triamine, tripropylene tetramine, bis-(3-aminopropyl)-amine, bis-(3-aminopropyl)methylamine, piperazine, 1,4-diaminocyclohexane, isophorone diamine, N-cyclohexyl-1,3-propane diamine, bis-(4-aminocyclohexyl)-methane, bis-(4-amino-3-methyl-cyclohexyl)-methane, bisaminomethyltricyclodecane (TCD diamine), o-, m- and p-phenylene diamine, 1,2-diamino-3-methylbenzene, 1,3-diamino-4-methylbenzene (2,4-diaminotoluene), 1,3-bisaminomethyl-4,6-dimethylbenzene, 2,4- and 2,6-diamino-3,5-diethyltoluene, 1,4- and 1,6-diaminonaphthalene, 1,8- and 2,7-diaminonaphthalene, bis-(4-aminophenyl)-methane, polymethylene-polyphenylamine, 2,2-bis-(4-aminophenyl)-propane, 4,4'-oxybis-aniline, 1,4-butanediol-bis-(3-aminopropyl ether), hydroxyl group-containing polyamines such as 2-(2-aminoethylamino)-ethanol, carboxyl group-containing polyamines such as 2,6-diamino-hexanoic acid. Also amine group-containing polyethers, e.g. those based on polyethylene oxide, polypropylene oxide or polytetrahydrofuran with a concentration of primary or secondary amine groups of 0.25 to about 6 mmol/g, preferably 1 to 6 mmol/g. These types of amine group-containing polyethers are commercially available (e.g. Jeffamin D-400, D-2000, DU-700, ED-600, T-403 and T-3000 from the Texaco Chem. Co.).

Particularly preferred polyamines are hydrazine, ethylene diamine, 1,2-propylene diamine, 1,3-propylene diamine, 1-amino-3-methylaminopropane, 1,4-diaminobutane, N,N'-dimethyl-ethylene diamine, 1,6-diaminohexane, diethylene triamine, N,N',N"-trimethyldiethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, polyethylene imine with molecular weights between 250 and 10,000, dipropylene triamine, tripropylene tetramine, isophorone diamine, 2,4-diaminotoluene and 2,6-diaminotoluene, bis-(4-aminophenyl)-methane, polymethylene-polyphenylamine and amine group-containing polyethers, e.g. those based on polyethylene oxide, polypropylene oxide, with a concentration of primary or secondary groups of 1 to 8 mmol/g.

Very particularly preferred polyamines are ethylene diamine, 1,2-propylene diamine, 1,3-propylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, polyethylene imine with a molecular weight between 250 and 10,000, 2,4-diaminotoluene and 2,6-diaminotoluene, bis-(4-amino-phenyl)-methane and polymethylene-polyphenylamine and also amine group-containing polyethers, e.g. those based on polyethylene oxide, polypropylene oxide, with a concentration of primary or secondary amine groups of 1 to 8 mmol/g and molecular weights between 250 and 2000.

In addition to polyamines, monoamines such as ammonia,  $C_1$  to  $C_{18}$  alkyl amines and di-( $C_1$  to  $C_{18}$  alkyl) amines and also aryl amines such as aniline,  $C_1$ - $C_{12}$  alkylaryl amines and aliphatic, cycloaliphatic or aromatic mono, di or poly  $C_1$  to  $C_{18}$  alcohols, aliphatic, cycloaliphatic or aromatic mono, di or  $C_1$  to  $C_{18}$  carboxylic acids, aminosilanes such as 3-aminopropyltrimethoxysilane and 3-aminopropyltriethoxysilane, and also polyethers and polyesters with molecular weights between 200 and 10,000 which have hydroxyl and/or carboxyl groups able to react with polyisocyanates, may also be used. Examples of these monoamines which may also be used are ammonia, methylamine, dimethylamine, dodecylamine, octadecylamine, ethanolamine, diethanolamine, beta-alanine or aminocaproic acid. The amount of these additional amines, alcohols, carboxylic acids, hydroxyl and/or carboxyl group-containing polyethers and polyesters depends on their concentration of groups able to react with polyisocyanates and is 0 to 0.5 mol of reactive groups per isocyanate equivalent.

Polyurea fillers according to the invention may, as mentioned, be prepared by reacting at least one polyisocyanate with at least one polyamine and/or water at temperatures of -50 to 250°C, preferably 20 to 150°C, in a solvent with precipitation of the polyurea. Preferred solvents and precipitating agents, apart from water, are aprotic solvents, in particular hydrocarbons such as butane, pentane, n-hexane, cyclohexane, n-octane, isooctane, benzene, toluene, xylene and/or chlorobenzene.



In the dry state, the polyurea fillers are present in an aggregated form. The aggregates can be broken up by mechanical processing, e.g. in a compounder. The particle size can be determined, for example, by electron microscopy, light scattering or ultracentrifuging.

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A particularly beneficial process for preparing polyurea-filled rubbers is characterised in that at least one polyisocyanate is reacted with at least one polyamine and/or water in a solvent with precipitation of the polyurea, a solution of a rubber is added thereto and the solvent is removed. The polyurea filler is preferably prepared directly in the rubber solution. This process has the advantage that the polyurea filler is produced immediately with the required particle size.

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The concentration of rubber in the solution may vary over wide limits and is generally 1 to 50 wt.%, preferably 5 to 30 wt.%. For economic reasons, the highest possible concentration of rubber in the solution is preferred.

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The polyisocyanate is preferably reacted with the polyamine in such a way that the polyisocyanate is initially introduced in the solvent or in an emulsion of solvent and water and the polyamine is then admixed, or the polyamine is initially introduced in the solvent or in an emulsion of solvent and water and the polyisocyanate is then admixed, and the rubber solution is added thereto. In a particularly preferred embodiment, the reaction is performed in the rubber solution or in an emulsion of the rubber solution and water. The amounts of polyisocyanate, polyamine and optionally water are governed by the degree of filling required in the resulting rubber mixture and by the desired properties of the polyurea filler which may still contain, for example, bonded amine groups when an excess of polyamine is used or bonded isocyanate groups when an excess of polyisocyanate is used.

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Preferred relative amounts of polyisocyanate and polyamine are 0.7 to 1.3, in particular 0.8 to 1.2 mol of isocyanate groups per mol of amine groups. Water may optionally be

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used in large excess either as solvent or emulsifier or also for reaction because it leads to the formation of amine groups from isocyanate groups which then react further with the remaining isocyanate groups.

5 To regulate the polyurea particle size, emulsifiers and dispersants are added before or during the preparation process. Suitable emulsifiers and dispersants are those with an anionic, cationic or non-ionic character such as the Na salt of dodecylbenzenesulfonic acid, dioctyl sulfosuccinate, the Na salt of naphthalenesulfonic acid, triethylbenzylammonium chloride or polyethylene oxide ethers such as the reaction  
10 products of nonylphenol with 3 to 50 mol of ethylene oxide per mol of nonylphenol, The amounts of emulsifiers or dispersants are about 0.1 to 5 wt.%, with respect to the total amount of polyurea.

The reaction times for the process according to the invention are between a few seconds  
15 and several hours.

The rubber solution, before during or after production of the polyurea filler, apart from the rubber, may also contain fillers, in particular carbon black and/or silica, and also rubber auxiliary substances such as mineral oils, pigments and stabilisers. Preferred  
20 amounts of carbon black are 0.1 to 100 parts by wt., of mineral oils are 0.1 to 50 parts by wt. and of stabilisers are 0.1 to 3 parts by wt., each with respect to 100 parts by wt. of rubber.

Both natural rubbers and synthetic rubbers are suitable for preparing rubber mixtures  
25 with polyurea fillers according to the invention.

Preferred synthetic rubbers are, for example, those described in W. Hofmann, Kautschuktechnologie, Gentner Verlag, Stuttgart 1980 and I. Franta, Elastomers and Rubber Compounding Materials, Elsevier, Amsterdam 1989. They include, inter alia,

	BR	polybutadiene
	ABR	butadiene/C <sub>1</sub> -C <sub>4</sub> alkyl acrylate copolymers
	CR	polychloroprene
	IR	polyisoprene
5	SBR	styrene/butadiene copolymers with styrene contents of 1-60, preferably 20-50 wt.%, and optionally 0 to 10 wt.% of polar unsaturated monomers such as (meth)acrylic acid, hydroxyethyl (meth)acrylate, acrylonitrile or vinylpyridine
10	IIR	isobutylene/isoprene copolymers with isoprene contents of 0.01 to 5 wt.% (butyl rubbers)
	BR-IIR	brominated isobutylene copolymers with bromine contents between 0.01 and 4 wt.% (bromobutyl rubber)
	Cl-IIR	chlorinated isobutylene copolymers with chlorine contents between 0.01 and 4 wt.% (chlorobutyl rubber)
15	IMS	isobutylene/p-methylstyrene copolymers
	BIMS	brominated copolymers with 0.05 to 3 mol.% of benzylically bonded bromine
20	NBR	butadiene/acrylonitrile copolymers with acrylonitrile contents of 5-60, preferably 10-40 wt.% and optionally 0 to 10 wt.% of other polar unsaturated monomers such as (meth)acrylic acid, hydroxyethyl (meth)acrylate or vinylpyridine
	HNBR	partially hydrogenated or fully hydrogenated NBR rubbers
	EPM	ethylene/propylene copolymers
25	EPDM	ethylene/propylene/diene copolymers with diene contents between 0.1 and 20 wt.%, preferably 0.5 to 10 wt.%
	FKM	fluorinated rubbers
	CO	polyepichlorhydrin
	ECO	copolymers of epichlorhydrin and ethylene oxide
30	EAM	ethylene/vinyl acetate copolymers with vinyl acetate contents of 20 to 90 wt.%, preferably 40 to 80 wt.%

MQ, VMQ    silicone rubbers

and also mixtures of these rubbers. Natural rubber, polyisoprene, emulsion SBR and solution SBR rubbers with a glass transition temperature higher than  $-50^{\circ}\text{C}$ , which may optionally be modified with functional groups as described, for example, in EP-A 447 066 (silyl groups), GB-A 2,085,896 (Sn groups), DE-A 19,832,458 (hydroxyl groups) and German patent application no. 19 852 648.2 (carboxyl groups), polybutadiene rubbers with a high 1,4-cis content ( $>90\%$ ), which have been prepared using catalysts based on Ni, Co, Ti or Nd, and also polybutadiene rubbers with a vinyl content of up to 75 %, butyl rubber, bromobutyl rubber, chlorobutyl rubber and mixtures of these are particularly useful for preparing vehicle tyres which contain fillers according to the invention.

Apart from the polyurea fillers, rubber mixtures according to the invention may also contain other fillers. Suitable other fillers for rubber mixtures according to the invention are any known fillers which are known in the rubber industry, these including both active and inactive fillers.

The following may be mentioned:

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- highly disperse silicas prepared, for example, by precipitation from solutions of silicates or by flame hydrolysis of silicon halides with specific surface areas of 5 - 1000, preferably 20-400  $\text{m}^2/\text{g}$  (BET surface area) and with primary particle sizes of 10-400 nm. Optionally, the silica may also be present as a mixed oxide with other metal oxides such as Al, Mg, Ca, Ba, Zn, Zr, Ti oxides;
- synthetic silicates such as aluminium silicate, alkaline earth silicates such as magnesium silicate or calcium silicate with BET surface areas of 20-400  $\text{m}^2/\text{g}$  and primary particle diameters of 10-400 nm;
- natural silicates such as kaolin and other naturally occurring silicas;

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- glass fibres and glass fibre products (mats, ropes) or glass microbeads;
- metal oxides such as zinc oxide, calcium oxide, magnesium oxide, aluminium oxide;
- metal carbonates such as magnesium carbonate, calcium carbonate, zinc carbonate;
- metal hydroxides such as e.g. aluminium hydroxide, magnesium hydroxide;
- carbon black. The carbon blacks used here are prepared by the lamp black, furnace black or channel black method and have BET surface areas of 20 to 200 m<sup>2</sup>/g, e.g. SAF, ISAF, HAF, FEF or GPF carbon black.

Highly disperse silica and/or carbon black are preferred as additional fillers, wherein the mixing ratio of polyurea filler to carbon black and/or silica is 1 : 0.05 to 30, particularly preferably 1 : 0.1 to 10.

Rubber mixtures according to the invention may also contain other rubber auxiliary substances which, for example, are used to cross-link the rubber mixtures, or which improve the physical properties of the vulcanisates prepared from rubber mixtures according to the invention for the specific ultimate purpose.

Sulfur or sulfur-providing compounds or peroxides are used as cross-linking agents. Sulfur or sulfur-providing compounds are particularly preferably used in amounts of 0.01 to 3 parts by wt., with respect to 100 parts by wt. of rubber. In addition, as mentioned above, rubber mixtures according to the invention may also contain further auxiliary substances such as known reaction accelerators, antioxidants, thermal stabilisers, light protection agents, ozone protection agents, processing auxiliary substances, reinforcing resins, e.g. phenol resins, steel wire bonding agents such as silica/resorcinol/hexamethylenetetramine or cobalt naphthenate, plasticisers, tackifiers, blowing agents, colorants, pigments, waxes, extenders, organic acids, delayers, metal

oxides and filler activators, in particular polysulfidic silanes such as bis-(triethoxysilylpropyl) tetrasulfide.

5 Rubber auxiliary agents according to the invention are used in conventional, known amounts, wherein the amount used is governed by the subsequent ultimate use of the rubber mixtures. Conventional amounts of rubber auxiliary substances are, for example, in the range 2 to 70 parts by wt., with respect to 100 parts by wt. of rubber.

10 Rubber mixtures according to the invention may also be prepared by mixing the rubber with the separately prepared polyurea fillers and optionally other fillers, rubber auxiliary agents and cross-linking agents in suitable mixing equipment such as compounders, rollers or extruders. The rubber/polyurea mixture is very particularly prepared from the rubber solution by the preparation process according to the invention.

15 The present invention also provides use of rubber mixtures according to the invention to produce vulcanisates and highly reinforced rubber moulded items, preferably for the preparation of low rolling resistance tyre treads, in particular those based on BR, IR, NR or SBR rubbers, low-damping tyre side-walls for tyres with emergency running properties, as described in US-A 5 368 082, 5 427 166, 5 511 599 and EP-A 475 258,  
20 and also gas-tight and low-damping tyre inners, in particular those based on butyl, bromobutyl or chlorobutyl rubbers.

The rubber mixtures are preferably used to produce tyres and industrial rubber items.

25 The present invention also provides rubber vulcanisates, rubber moulded items of all types, in particular tyres and industrial rubber items, which are produced in a conventional manner using rubber mixtures according to the invention.

**Examples****Example 1: Mixture of S-SBR and 50 phr of a polyurea filler based on TDI**

5 186.2 g of Desmodur T 80 (toluylene-2,4/2,6 diisocyanate mixture (80:20) from Bayer AG) were added to a solution of 500 g of Buna VSL 5025-0 (solution SBR with 25 wt.% of bonded styrene, Bayer AG) in 4 l of cyclohexane. Then, with stirring (150 rpm) at 60°C, 64.2 g of ethylene diamine were added over 5 minutes and stirring was continued for one hour at 80°C. A homogeneous dispersion of polyurea particles with a  
10 particle diameter between 0.1 and 6 µm, 50 % of which particles were ≤ 0.8 µm (measured by ultracentrifuging), was produced. Then 2.5 g of antioxidant Vulkanox 4020 (Bayer AG) were stirred in. Finally, the solvent was distilled off with steam (105°C). After drying at 70°C under vacuum, 746 g of homogeneous polyurea-filled S-SBR rubber mixture with the viscosity ML 1+4 (100°C) of 110 were obtained. The  
15 polyurea filler had a melting or decomposition point >240°C (by DSC). The glass transition temperature of the rubber mixture was -19°C, the polyurea filler did not have a glass transition temperature.

**Example 2: Mixture of polybutadiene rubber and 50 phr of polyurea filler based  
20 on TDI**

147.9 g of Desmodur T 80 (toluylene-2,4/2,6 diisocyanate mixture (80:20) from Bayer AG) were added to a solution of 400 g of Buna CB 25 (polybutadiene rubber, Nd type, Bayer AG) in 4 l of cyclohexane. Then, with stirring (150 rpm) at 60°C, 51 g of ethylene diamine were added over 10 minutes. Stirring was continued for one hour at 80°C. A  
25 homogeneous dispersion of polyurea particles with a particle diameter between 0.1 and 6 µm (measured by ultracentrifuging), was produced. Then 2 g of antioxidant Vulkanox 4020 (Bayer AG) were stirred in. Finally, the solvent was distilled off with steam (105°C). After drying at 70°C under vacuum, 596 g of homogeneous polyurea-filled BR rubber mixture with the viscosity ML 1+4 (100°C) of 160 were obtained.

**Example 3: Mixture of S-SBR and 50 phr of polyurea filler based on MDI**

201.8 g of Desmodur 44 M (4,4'-diphenylmethane diisocyanate from Bayer AG) were added to a solution of 500 g of Buna VSL 5025-0 (solution SBR with 25 wt.% of bonded styrene, Bayer AG) in 4 l of cyclohexane. Then, with stirring (100 rpm) at 60°C, 48.4 g of ethylene diamine were added over 5 minutes and stirring was continued for one hour at 80°C. A dispersion of polyurea particles with a particle diameter between 0.1 and 6 µm (measured by ultracentrifuging), was produced. Then 2.5 g of antioxidant Vulkanox 4020 (Bayer AG) were stirred in. Finally, the solvent was distilled off with steam (105°C). After drying at 70°C under vacuum, 750 g of homogeneous polyurea-filled S-SBR rubber mixture were obtained.

**Example 4: Mixture of butyl rubber and 50 phr of polyurea based on TDI**

400 ml of water and 32.1 g of ethylene diamine were added to a solution of 250 g of Polysar Butyl 402 (butyl rubber with 2.2 mol.% of residual double bonds, ML 1+4 (125°C): 33, Bayer AG) in 2 l of cyclohexane. Then, 93.1 g of Desmodur T 80 (toluylene diisocyanate-2,4/2,6 diisocyanate mixture (80:20), Bayer AG) were added dropwise to this mixture over the course of 10 minutes, with stirring (200 rpm) and at 40°C and stirring was continued for one hour at 80°C. A finely divided, white dispersion with a particle size between 1 and 50 µm (measured by ultracentrifuging) was produced. Then 1 g of Vulkanox 4020 (stabiliser from Bayer AG) was added and the solvent was distilled off with steam. After drying at 70°C under vacuum, a snow-white rubber mixture with 50 phr of polyurea filler and a viscosity ML 1+4 (100°C) of 96 was obtained.

**Example 5: Mixture of hydrogenated NBR rubber and 25 phr of polyurea based on TDI and diethylene triamine**

300 ml of water and 26.6 g of diethylene triamine were added to a solution of 375 g of



HNBR rubber Therban C 3467 (HNBR with a 34 % acrylonitrile content, 5.5 % of residual double bonds, Bayer AG) in 3 l of chlorobenzene. Then, 67.2 g of Desmodur T 80 (toluylene diisocyanate-2,4/2,6 diisocyanate mixture (80:20), Bayer AG) were added dropwise to this mixture over the course of 10 minutes, with stirring (160 rpm) and at 5 60°C and stirring was continued for one hour at 80°C. A finely divided, white dispersion with a particle size between 1 and 50 µm (measured by light microscopy) was produced. Then 1 g of Vulkanox 4020 (stabiliser from Bayer AG) was added and the solvent was distilled off with steam. After drying at 70°C under vacuum, a white HNBR rubber mixture with 25 phr of polyurea filler and a viscosity ML 1+4 (100°C) of 10 120 was obtained.

**Examples 6 to 12: Further polyurea-filled rubber mixtures**

The same procedure was used as described in the preparative process in example 1, 15 wherein the following rubbers, solvents, polyisocyanates and polyamines were used. The mixtures were stabilised, as in example 1, by adding 2.5 g of Vulkanox 4020 (Bayer).

Ex. no.	Rubber	Solvent	Polyisocyanate	Polyamine	Dispersion		End product	
					Appearance under optical microscope	Particle size after ultracentrifuging	Filler conc.	ML 1+4 (100°C)
6	Butyl rubber butyl 402 (Bayer) (2.2% res. double bond content) 500 g	Cyclohexane 4 l	Tolylene diisocyanate Desmodur T80 (Bayer AG) 372.4 g (2.14 mol)	Ethylene diamine 128.4 g (2.14 mol)	finely divided homogeneous dispersion with no coarse fraction (>20 µm)	0.1 - 6 µm	100 phr	135
7	EPDM rubber Buna EP T 2450 (Bayer) (4 % ENB conc. Ethylene conc. 59 %) 500 g	Cyclohexane 4 l	Tolylene diisocyanate Desmodur T80 (Bayer AG) 99.2 g (0.53 mol)	Ethylene diamine 31.8 g (0.53 mol)	finely divided homogeneous dispersion with no coarse fraction (>20 µm)	0.1 - 6 µm	24.8 phr	62
8	EPDM rubber Buna EP T 2450 (Bayer) (4 % ENB conc. Ethylene conc. 59 %) 500 g	Cyclohexane 4 l	Tolylene diisocyanate Desmodur T80 (Bayer AG) 186.2 g (1.07 mol)	Ethylene diamine 64.2 g (1.07 mol)	finely divided homogeneous dispersion with no coarse fraction (>20 µm)	0.1 - 6 µm	50 phr	101
9	S-SBR rubber Buna VSL 5025-0 (Bayer) (25 wt. % styrene, 50 wt. % 1,2-bonded butadiene) 500 g	Cyclohexane 4 l	Tolylene diisocyanate Desmodur T80 (Bayer AG) 179.2 g (1.03 mol)	Diethylene triamine 70.7 g (0.686 mol)	finely divided homogeneous dispersion with no coarse fraction (>20 µm)	0.1 - 6 µm	50 phr	132
10	S-SBR rubber Buna VSL 5025-0 (Bayer) (25 wt. % styrene, 50 wt. % 1,2-bonded butadiene) 500 g	Cyclohexane 4 l	Hexamethylene diisocyanate 177.5 g (1.055 mol)	Diethylene triamine 72.4 g (1.055 mol)	finely divided homogeneous dispersion with coarse fraction (20 - 100 µm)		50 phr	115
11	S-SBR rubber Buna VSL 5025-0 (Bayer) (25 wt. % styrene, 50 wt. % 1,2-bonded butadiene) 500 g	Cyclohexane 4 l	Desmodur N 3200 (Bayer), polyisocyanate based on HDI with 23 wt. % NCO 210.3 g (1.15 mol NCO)	Diethylene triamine 39.6 g (0.38 mol)	finely divided homogeneous dispersion with no coarse fraction (>20 µm)	0.1 - 6 µm	50 phr	100
12	Ethylene/vinyl acetate rubber Levapren 450 (Bayer) (45 % vinyl acetate, ML 1+4 (100°C): 20 500 g	Cyclohexane 4 l	Tolylene diisocyanate Desmodur T80 (Bayer AG) 186.2 g (1.07 mol)	Ethylene diamine 64.2 g (1.07 mol)	finely divided homogeneous dispersion particle size 1 - 15 µm		50 phr	46

**Claims**

1. Rubber mixtures consisting of a rubber and 1 to 300 parts by wt., with respect to 100 parts by wt. of rubber, of a polyurea filler with a particle size of 0.001 to 500  $\mu\text{m}$  and optionally further rubber auxiliary substances and cross-linking agents.  
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2. Rubber mixtures as claimed in Claim 1, wherein the rubber mixtures contain 5 to 150 parts by wt. of polyurea filler, with respect to 100 parts by wt. of rubber.  
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3. A process for preparing polyurea-filled rubber mixtures as claimed in Claim 1, wherein a polyisocyanate is reacted with a polyamine and/or water at temperatures of  $-50$  to  $250^{\circ}\text{C}$  in a solvent with precipitation of the polyurea, a solution of a rubber is added to the polyurea obtained and the solvent is removed.  
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4. A process as claimed in Claim 3, wherein the polyisocyanate is reacted with the polyamine in a solution of the rubber or in an emulsion of the rubber solution and water.  
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5. A process as claimed in Claim 3, wherein the relative amounts of polyisocyanate used to polyamine used is 0.7 to 1.3 mol of isocyanate groups per mol of amine groups and the water is optionally used in large excess.
- 25 6. Use of rubber mixtures as claimed in Claim 1 to produce moulded items and vulcanisates, in particular to produce industrial rubber articles and tyres.
7. Vulcanisates, in particular industrial rubber articles and tyres, obtainable by using rubber mixtures as claimed in Claim 1.  
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**Rubber mixtures with polyurea mixtures**

Abstract

- 5 Rubber mixtures according to the invention consist of rubber and specific polyurea fillers with a particle size of 0.001 to 500  $\mu\text{m}$  and are particularly suitable for producing rubber vulcanisates and rubber moulded items with low specific weights and low dynamic damping, in particular for producing low-damping tyres. Furthermore, they can be used in industrial rubber articles with a demanding range of physical requirements.

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